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Two synthetic routes to bis(1-methyl-imidazole-2-thione)methane and bis(1-benzyl-imidazole-2-thione)methane complexes including sulfur atom insertion into copper−NHC bonds

Miriam Slivarichova,[b] Rosenildo C. da Costa,[a] Joshua Nunn, [b] Ruua Ahmad,[b] Mairi F. Haddow,[b] Hazel A. Sparkes,[b] Thomas Gray,[b] and Gareth R. Owen*[a,b]

Dedicated to Professor John A. Gladysz on the occasion of his 65th birthday.

Keywords: NHCs / Thiones / Copper / Sulfur atom insertion / Crystallography

[a] The School of Applied Science, Univeristy of South Wales, Treforest, UK, CF37 4AT
Tel: 01443 654527 E-mail: gareth.owen@southwales.ac.uk
[b] The School of Chemistry, University of Bristol, Cantock's Close, Bristol, UK, BS8 1TS

The synthesis of novel bis-thione ligand, bis(1-benzyl-imidazole-2-thione)methane, **SS^{Bn}** is reported for the first time. This ligand along with the previously reported bis(1-methyl-imidazole-2-thione)methane, **SS^{Me}** has been utilised in the synthesis of a series of copper(I) halide complexes. The syntheses have been achieved by two methodologies. The first method involves the direct addition of the ligands to the copper halide salts, CuCl, CuBr and CuI. The second methodology involves an insertion of a sulfur atom into the copper–NHC bond of the preformed organometallic complexes, [CuBr(**CS^{Me}**)]$_2$ and [CuI(**CS^{Me}**)]$_2$ {where **CS^{Me}** = 1-(3-methyl-2H-imidazol-1-yl-2-thione)methyl-3-methyl-2H-imidazol-2-ylidene} and [CuBr(**CS^{Bn}**)]$_2$ and [CuI(**CS^{Bn}**)]$_2$ {where **CS^{Bn}** = 1-(3-benzyl-2H-imidazol-1-yl-2-thione)methyl-3-benzyl-2H-imidazol-2-ylidene}. These sulfur atom insertion reactions provide an indirect route to the first copper−halide complexes containing the **SS^{Me}** and **SS^{Bn}** ligands. All six complexes prepared have been fully characterized by spectroscopic and analytical methods as well as X-ray crystallography. Dinuclear structures were obtained for the complexes containing **SS^{Me}**, mononuclear complexes were obtained for the copper–chloride and copper–bromide complexes containing **SS^{Bn}** and an extended network containing [Cu$_4$I$_4$] clusters bridged by the **SS^{Bn}** were formed for the corresponding copper–iodide complex for the latter ligand. The coordination and structural features of the two bis-thione ligands are discussed.

1. Introduction

There has been a significant and long standing interest in the 1-R-imidazole-2-thione heterocycle (H**mt^R**, where the R group is an alkyl or aryl group) and its incorporation within polydentate ligand motifs (Figure 1).[1] Much of this work has focused on anionic so-called "flexible soft scorpionate ligands" which contain a borohydride bridging unit between the heterocycles, for example [**Tm**]$^-$ and [**Bm**]$^-$ where R = Me in Figure 1.[2] Neutral bidentate and tridentate ligands bridged by CH_2 and CH units have also been extensively studied.[3,4]

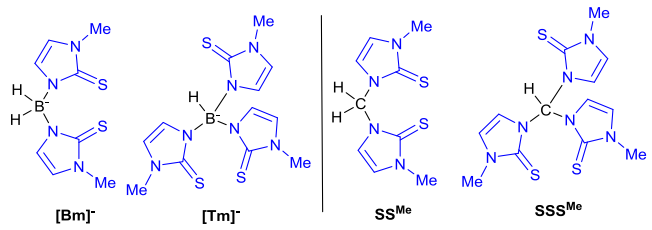


Figure 1 – Bidentate and tridentate ligands containing two or three of the methyl substituted 1-R-imidazole-2-thione units. The anionic ligands, bridged by borohydride are shown on the left and neutral ligands featuring CH_2 and CH units are shown on the right.

In a recent publication, we coordinated bis(1-methyl-imidazole-2-thione)methane (**SS^{Me}**) to a series of zinc salts.[3n] This ditopic ligand has previously been utilised to prepare a wide range of complexes in which it exhibits a range of different coordination modes, some of which are highlighted in Figure 2. Examples of complexes containing **SS^{Me}** have been reported with d-block metals such as silver,[3f,o] gold,[3o] rhodium,[3g,k,l] iridium,[3l] nickel,[3j] iron,[3m] cobalt,[3j] zinc,[3n,q] and rhenium[3h] in addition to other metals such as tin,[3d] lead[3c,i], antimony[3a] and bismuth.[3a,r] The ligand has a number of interesting features. The number of atoms from one sulfur to the other is seven. This means that for a κ^2-*SS* coordination mode an eight-membered metallacycle is formed with the metal centre. This ring size is larger than normally found in most compounds containing chelating ligands. One of the consequences of this larger chelation size has been a positioning of the central methylene unit in close proximity to the metal centre (Figure 3). This is demonstrated in the complexes [Rh(COD)(κ^2-*SS*-**SS^{Me}**)]X (where X = $[PF_6]^-$ and $[BF_4]^-$), published in 2006 by Hill.[3g] The ligand in this complex adopts a weak interaction between one of the hydrogen atoms on the central CH_2 unit of the ligand and the rhodium centre at lower temperatures in solution as well as in the solid state. While the C–H–Rh interaction is relatively long for the **SS^{Me}** ligand, the

corresponding B–H–Rh interaction in the related complex [Rh(COD)(κ²-*SS*-**Bm**)] was found to be significantly shorter.[5] The activation of the B–H bond in the borohydride based ligands is now well established leading to the formation of metal–borane (σ–acceptor) complexes.[2a,6] On the other hand, the activation of a C–H bond in the **SS^{Me}** ligand, is unknown although there are rare examples of related compounds where activation has been observed.[7]

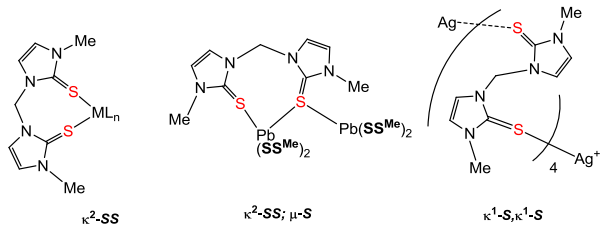


Figure 2 – Highlighting the diverse range of coordination modes of **SS^{Me}**. There are many examples of complexes featuring the κ²-*SS* (see main text for details).

Other features of the ligands include the ability to bridge two metal centres, either via the two lone pairs on an individual sulfur donor (μ–*S*), bridging two metal centres via κ¹,κ¹ modes (*i.e.* one metal at each sulfur) or a combination of the two bridging types as shown in the silver and lead complexes in Figure 2.

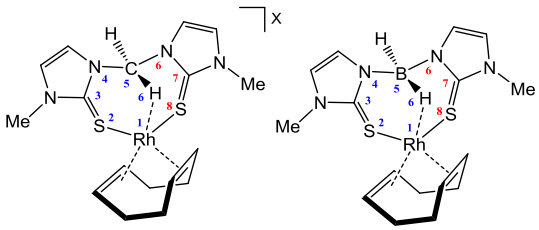


Figure 3 – The coordination of **SS^{Me}** to the rhodium centre in [Rh(COD)(κ²-*SS*-**SS^{Me}**)]X (where X =PF_6 and BF_4), highlighting the eight membered ring formed by the presence of the κ²-*SS* coordination mode versus the two six membered rings formed by the E–H–Rh interactions.

In a related study, we have also investigated the coordination properties of a novel family of ditopic ligands, the first to contain both thione and NHC donor functionalities within the same ligand (*e.g.* **CS^{Me}** and **CS^{Bn}** in Figure 4).[8] It is worthy to note that these ligands differ from **SS^{R}** only by the absence of one sulfur atom. Several organometallic complexes were prepared using this mixed donor ligand. Indeed, these ligands were also found to exhibit a range of different coordination motifs. The copper complexes containing the **CS^{R}** ligands formed dimeric 'CuSCuS' cores where the ligands were attached with intermediate coordination modes, somewhere between κ¹-*C*,κ¹-*S* and κ²-*CS*.[8a] The 'CuSCuS' bridging interactions in these complexes ranged from weak to strong depending on the halide. On the other hand, the complexes containing the ligands in the silver complexes formed well-defined κ²-*CS* motifs.[8b] As indicated in Figure 2, some silver complexes containing **SS^{Me}** have previously been reported by Gardinier *et al.*[3f]

Even though there is a diverse range of complexes containing the **SS^{Me}** ligand, until recently there had been no structurally characterised examples of any copper complexes. Bark *et al.* had previously reported that this ligand coordinated to copper metal centres[3b] indicating that 1:1 complexes may have been formed with **SS^{Me}** and copper(I) salts. However, no further details were provided. In 2015, Brumaghim reported the first structurally characterised copper complexes to contain **SS^{Me}**. The complex $[Cu_2(\mathbf{SS^{Me}})_3][BF_4]_2$ was prepared along with two others which contained **SS^{Me}** in addition to other derivative ligands.[3p] To the best of our knowledge, there are currently no reported copper–halide complexes containing **SS^{Me}**. Furthermore, the synthesis of the related ligand, **SS^{Bn}**, is unknown. Accordingly, we wish to report the first copper–halide complexes (chloride, bromide and iodide) of both **SS^{Me}** and **SS^{Bn}** ligands. We report the synthesis of the complexes via two different synthetic routes. The preparation of these complexes was achieved by direct coordination of the respective ligand to copper(I) salt. A second route was an indirect method via addition of elemental sulfur to the corresponding organometallic complexes $[CuX(\mathbf{CS^{R}})]_2$ (where R = Me, Bn; X = Br, I). This latter reactivity involves the insertion of a sulfur atom into the copper–*N*-heterocyclic carbene bond.

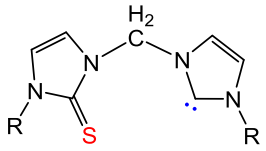
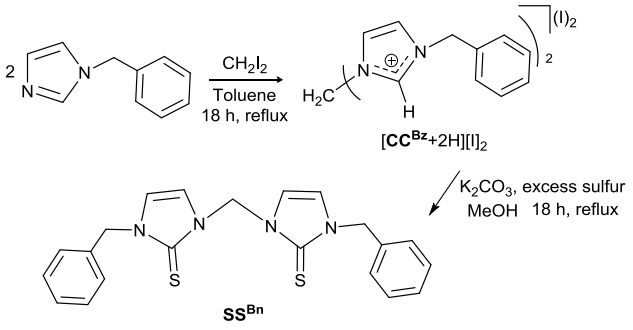


Figure 4 – Mixed bidentate **CS^{R}** ligands containing thione and *N*-heterocyclic carbene ligands (where R = Me, Bn).

2. Results and Discussion

2.1 Synthesis of bis(1-benzyl-imidazole-2-thione)methane (SS^{Bn})

The syntheses of various substituted bis(1-R-imidazole-2-thione)methanes (**SS^{R}**; where R = Me, ^{t}Bu and ^{i}Pr) have already been established.[3a,m] On the other hand, the corresponding species bis(1-benzyl-imidazole-2-thione)methane (**SS^{Bn}**) has not previously been reported. Accordingly, we decided to synthesise it as a new example. The ligand was readily prepared via an analogous route to previous examples from 1,1-dibenzyl-3,3-methylenediimidazolium diiodide[9] (via *N*-benzylimidazole and diiodomethane). The diiodide imidazolium salt was reacted with elemental sulfur and potassium carbonate in refluxing methanol for 24 h to give the final product **SS^{Bn}** (Scheme 1). The product obtained was recrystallised from methanol and isolated in excellent yield. The crystalline solids were fully characterized by spectroscopic and analytical methods. The ^{1}H NMR spectrum in $CDCl_3$ confirmed the loss of both imidazolium protons. One singlet was observed for the methylene unit at 6.41 ppm, integrating for two protons, and a signal at 5.22 ppm was observed for the benzyl CH_2 units. The latter signal integrated to four protons again confirming incorporation of two thione units into the product. The $^{13}C\{^{1}H\}$ NMR spectra showed a characteristic signal at 164.0 ppm confirming the presence of the C=S groups in the new compound. Mass spectrometry and elemental analysis were also consistent with the formation of the targeted product.

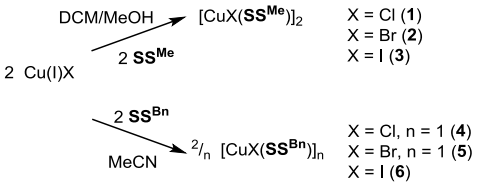


Scheme 1 – Synthesis of bis(1-benzyl-imidazole-2-thione)methane (**SS^{Bn}**)

2.2 Synthesis of copper(I) complexes via a direct route

As it is a new ligand, the addition of bis(1-benzyl-imidazole-2-thione)methane to transition metal centres has not been studied. We therefore initiated an investigation into its coordination properties to the three copper(I) halide salts (CuCl, CuBr and CuI). We also

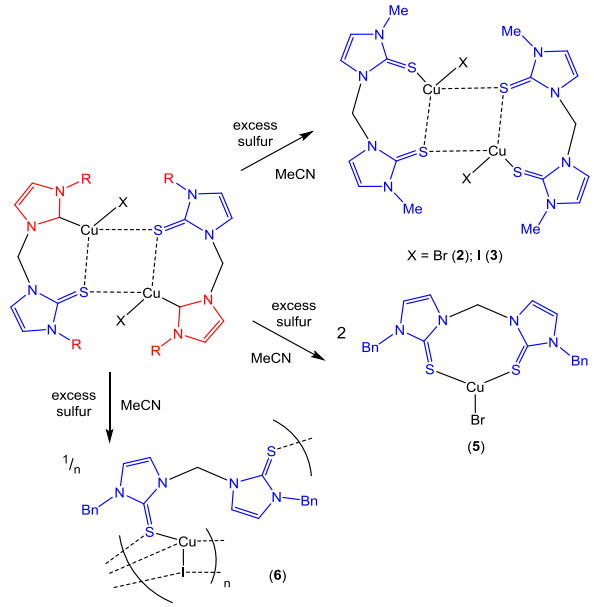
prepared the analogous $\mathbf{SS^{Me}}$ complexes via this same route. The series of complexes, $[CuCl(\mathbf{SS^{Me}})]_2$ (**1**), $[CuBr(\mathbf{SS^{Me}})]_2$ (**2**), $[CuI(\mathbf{SS^{Me}})]_2$ (**3**), $[CuCl(\mathbf{SS^{Bn}})]$ (**4**), $[CuBr(\mathbf{SS^{Bn}})]$ (**5**) and $[CuI(\mathbf{SS^{Bn}})]_n$ (**6**) were prepared as outlined in Scheme 2. The specific morphologies obtained for each complex are outlined below. Complexes **1**, **2** and **3** were prepared by addition of one equivalent of a dichloromethane solution of the ligand to a methanol solution of the corresponding copper halide. Within a few minutes, solid started to precipitate from the mixture. After 12 h, the products were isolated by filtration, washed with diethyl ether and dried under reduced pressure. Complexes **4**, **5** and **6** were readily prepared by addition of one equivalent of the ligand in acetonitrile to a solution of the corresponding copper(I) halide in the same solvent (Scheme 2). Again, within a few minutes, the solid started to precipitate from the mixture. After 12 h, the products were isolated using a similar work-up procedure as for **1**, **2** and **3**. The complexes were not particularly soluble in many standard organic solvents. The $\mathbf{SS^{Me}}$ complexes were more soluble in MeCN than the corresponding $\mathbf{SS^{Bn}}$ complexes. All complexes were soluble in DMSO.



Scheme 2 – Synthesis of $[CuX(\mathbf{SS^{Me}})]_n$ (**1** – **6**) via direct addition of $\mathbf{SS^R}$ to their respective copper(I) halides (X = Cl, Br, I).

2.3 Synthesis of copper(I) complexes via a sulfur atom insertion route

For a good reason, there is a strongly held acceptance that NHC ligands form very strong bonds to transition metals.[10] Despite this, we had previously demonstrated that the copper–carbon bond of complexes containing the $\mathbf{CS^R}$ ligands could be cleaved in the presence of oxygen to provide the corresponding 'oxidation product' 1-[(3-R-2-thioxo-2H-imidazol-1-yl)methyl]-3-R-2H-imidazol-2-one (*i.e.* $\mathbf{OS^R}$).[8a] Others have reported similar observations where imidazole-2-one functional groups have been formed, although such reactivity is very rare.[11] The copper metal centre itself seems to be crucial here since the oxidation products, $\mathbf{OS^R}$, have not been found to occur when the $\mathbf{CS^R}$ ligands are coordinated to any other transition metal centres that we have thus far tested (*i.e.* Pd, Rh, Ag). In the case of copper, the resulting $\mathbf{OS^R}$ species were found to be poor ligands resulting in demetallation. As it was apparent that formal insertion of oxygen could be achieved, we wondered whether it was possible to insert elemental sulfur into the copper–carbon bond. Insertion of elemental sulfur into metal–carbon bonds has previously been observed[12] as well as the reverse reactivity.[1c,13] It was of particular interest to us to test the possibility of providing an indirect route to complexes of the type $[CuX(\mathbf{SS^R})]_n$. Accordingly, the reaction of the $[CuX(\mathbf{CS^R})]_2$ precursors with elemental sulfur was explored. In order to test the feasibility of the reaction, small samples of $[CuX(\mathbf{CS^R})]_n$ (where X = Br, I and R = Me, Bn) were placed in NMR tubes in the presence of excess sulfur. DMSO-d_6 was added to dissolve the copper complexes. The mixtures were examined by ^{1}H NMR spectroscopy and the conversions to the desired sulfur insertion products were monitored. In all cases, conversion to the new products took place. At room temperature, the transformations were slow; however, upon heating the NMR tubes to 80 °C, they gave complete conversion to the sulfur insertion products. Successful generation of the new complexes led us to attempt to find a scaled up synthesis where the target product could be isolated. The poor solubility of the $[CuX(\mathbf{CS^R})]_n$ complexes hampered this synthesis somewhat. DMSO was not a suitable solvent for this scaled up synthesis since it was not able to isolate the product from solution despite several attempts. For this reason, we used acetonitrile as a solvent despite the fact that the $[CuX(\mathbf{CS^R})]_n$ complexes were only partially soluble (Scheme 3). A sample of $[CuBr(\mathbf{CS^{Me}})]_2$ was placed in acetonitrile and an excess of S_8 (20 equivalents of $^1/_8$ S_8 per $\mathbf{CS^{Me}}$ ligand) was added. The reactions were monitored by taking small aliquots of the mixture, evaporating the solvent and recording the ^{1}H NMR spectrum in DMSO-d_6 at regular intervals. There was approximately 20% conversion of the starting material after 1 h at room temperature. This increased to approximately 50% overnight after which time no further significant conversion was observed. In a separate experiment, a fresh mixture was heated to 50 °C for 3 h to afford full conversion of $[CuBr(\mathbf{CS^{Me}})]_2$ to the new more symmetrical product $[CuBr(\mathbf{SS^{Me}})]_2$. The new compound was isolated via a standard workup. Full characterisation (*vide infra*) revealed it to be the targeted species, *i.e.* the product of formal sulfur atom insertion into the copper–NHC bond (Scheme 3). The analogous reaction was attempted with $[CuI(\mathbf{CS^{Me}})]_2$ and elemental sulfur. In this case, the reaction proceeded at a slower rate. No conversion was observed at ambient temperatures, only approximately 15 % of the target product was observed after 3 h at 50 °C. Full conversion to $[CuI(\mathbf{SS^{Me}})]_2$ was only obtained after a further 3 h at 70 °C. For the reaction involving $[CuBr(\mathbf{CS^{Bn}})]_2$ and elemental sulfur, full conversion was obtained after 5 h at 70 °C and finally for $[CuI(\mathbf{CS^{Bn}})]_2$ full conversion was observed after 3 h at 70 °C. It appeared that the length of time required to reach full conversion products was related to the solubility of the starting complexes in acetonitrile. For all four reactions, the products were isolated via a standard workup with yields ranging from 44% to 66%.



Scheme 3 – Synthesis of dinuclear $[CuX(\mathbf{SS^{Me}})]_2$ (X = Br; **2** and X = I; **3**), mononuclear $[CuBr(\mathbf{SS^{Bn}})]$ (**5**) and polymeric mononuclear $[CuI(\mathbf{SS^{Bn}})]_n$ (**6**) via addition of elemental sulfur to $[CuX(\mathbf{CS^{Me}})]_2$ and $[CuX(\mathbf{CS^{Bn}})]_2$.

2.4 Characterisation of copper(I) complexes

The six complexes were fully characterised by spectroscopic and analytical techniques. The ^{1}H and ^{13}C{^{1}H} NMR spectra of the isolated solids in DMSO-d_6 confirmed that the target complexes were formed. Table 1 provides a comparison of the ^{1}H NMR spectroscopic data for these complexes together with both the free ligands and $[CuX(\mathbf{CS^R})]_2$ precursors used for the sulfur insertion reactions. The spectroscopic data for **1, 2** and **3** in solution were not consistent with their solid state structures which revealed dimeric structures (see structural characterisation below). Specifically, the ^{1}H and ^{13}C{^{1}H} NMR data in solution for these three complexes were consistent with the $\mathbf{SS^{Me}}$ ligand in a symmetrical environment. For example, there was only one chemical environment for the N–

CH_3 groups in the NMR. In the case of the methylene bridge, the C*H*$_2$ resonances were located as singlet signals at 6.49 ppm (**1**), 6.56 ppm (**2**) and 6.72 ppm (**3**) in the ^{1}H-NMR spectra. The coordination of the thione donors to the copper centres was confirmed in the ^{13}C{^{1}H} NMR spectra. The spectra revealed only one resonance for the coordinated thione unit at 158.2 ppm, 157.7 ppm and 155.6 ppm for **1** – **3**, respectively (for the *C*=S group) an upfield shift compared to 159.3 ppm for the free ligand. These chemical shifts are consistent with previously reported copper complexes containing thione functionalities.[3p,8a] The IR spectra of **1** – **3** also showed similar characteristic absorption bands shifted relative from the free ligand. Coordination to the metal centres was further confirmed by positive ESI-mass spectrometry which all showed the peak corresponding to the expected cations, $[Cu_2X(\mathbf{SS^{Me}})_2]^+$ resulting from loss of one halide ligand from the dinuclear species $[CuX(\mathbf{SS^{Me}})]_2$. Furthermore satisfactory elemental analysis was obtained for the three complexes confirming the 1:1 copper to ligand ratio. Similarly, complexes **4** – **6** were obtained as analytically pure white solids in high yields. The three compounds were characterised by spectroscopic and analytical methods. Again, the ^{1}H and ^{13}C{^{1}H} NMR data (in DMSO-d$_6$) for **4** – **6** were consistent with the coordination of the $\mathbf{SS^{Bn}}$ ligand to the copper centres with a symmetric coordination mode. In this case, this is consistent with the solid state structures (*vide infra*). The methylene resonances were located as singlet signals at 6.46 ppm (**4**), 6.66 ppm (**5**) and 6.65 ppm (**6**) in the ^{1}H-NMR spectra. These are shifted downfield with respect to the free ligand $\mathbf{SS^{Bn}}$ which is located at 6.21 ppm. Coordination of the ligand to the copper centres was further confirmed by ESI-mass spectrometry. Again, the ratio of metal to ligand was confirmed as 1:1 by elemental analysis.

Table 1 – A comparison of the NMR spectroscopic chemical shifts found in the $\mathbf{SS^R}$ ligands, $[CuX(\mathbf{CS^R})]_2$ complexes and complexes **1** – **6**.[a]

Ligand Precursor / Complex	^{1}H (ppm)				^{13}C{^{1}H} (ppm)			
	C*H*$_3$	C*H*$_2$Ph	NC*H*$_2$N	NC*H*C*H*N	*C*H$_3$	*C*H$_2$Ph	NCH$_2$N	*C*=S
$\mathbf{SS^{Me}}$	3.44	–	6.40	7.27 / 7.54	34.8	–	56.1	159.3
$[CuBr(\mathbf{CS^{Me}})]_2$	3.51 / 3.68	–	6.24	7.29 / 7.29 / 7.62 / 7.69	37.6 / 35.6	–	59.5	157.5
$[CuI(\mathbf{CS^{Me}})]_2$	3.54 / 3.71	–	6.23	7.30 / 7.32 / 7.58 / 7.62	37.5 / 35.6	–	59.4	158.4
$[CuCl(\mathbf{SS^{Me}})]_2$ (**1**)	3.41	–	6.49	7.31 / 7.32	35.5	–	56.5	158.2
$[CuBr(\mathbf{SS^{Me}})]_2$ (**2**)	3.48	–	6.56	7.35 / 7.36	35.6	–	56.2	157.7
$[CuI(\mathbf{SS^{Me}})]_2$ (**3**)	3.58	–	6.72	7.43 / 7.44	36.2	–	56.6	155.6
$\mathbf{SS^{Bn}}$	–	5.20	6.21	7.18 / 7.45	–	49.9	56.3	163.0
$[CuBr(\mathbf{CS^{Bn}})]_2$	–	5.23 / 5.26	6.26	7.39 / 7.39 / 7.62 / 7.66	–	51.0 / 53.6	59.6	158.9
$[CuI(\mathbf{CS^{Bn}})]_2$	–	5.25 / 5.33	6.26	7.38 / 7.40 / 7.62 / 7.64	–	51.1 / 53.3	59.7	159.0
$[CuCl(\mathbf{SS^{Bn}})]$ (**4**)	–	5.16	6.46	7.40 / 7.57	–	50.4	56.4	158.2
$[CuBr(\mathbf{SS^{Bn}})]$ (**5**)	–	5.22	6.66	7.50 / 7.70	–	50.3	56.2	159.4
$[CuI(\mathbf{SS^{Bn}})]_n$ (**6**)	–	5.20	6.65	7.46 / 7.67	–	50.7	56.0	157.5

[a] NMR experiments carried out in DMSO-d$_6$, the data for the $[CuX(\mathbf{CS^R})]_2$ complexes were obtained from reference 8a.

2. 5 Structural characterisation of copper complexes

Single crystals were obtained from samples of all six copper complexes (**1** – **6**) and X-ray diffraction studies were performed. The crystal structures obtained from each of the samples are shown in Figures 5 – 11. During the course of our investigations we also carried out a test reaction in which $\mathbf{SS^{Me}}$ was dissolved in DCM and a methanolic solution containing Cu[BF$_4$]$_2$.3H$_2$O was added as a layer above. Crystals were obtained after 18 h and the resulting material was characterized by X-ray diffraction. As shown in Figures 12 and 13, the compound was found to contain eight copper(I) centers joined by ten $\mathbf{SS^{Me}}$ ligands, *i.e.* $[Cu_8(\mathbf{SS^{Me}})_{10}][BF_4]_8$ (**7**). Selected bond lengths and distances are highlighted in Tables 2 for comparison of complexes **1**, **2** and **3**, Table 3 for comparison of complexes **4** and **5** and in the corresponding figure captions for complexes **6** and **7**. Crystallographic parameters for all complexes are provided in Tables S1 and S2 in the supplementary information.

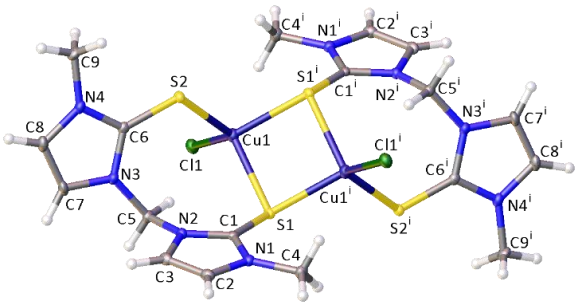


Figure 5 – Molecular structure of $[CuCl\{\kappa^2\text{-}SS,\mu\text{-}S\text{-}\mathbf{SS^{Me}}\}]_2$ (**1**) with atomic labelling scheme depicted. Ellipsoids shown at 50% probability level (^{i} = 1-*x*, 2-*y*, 1-*z*).

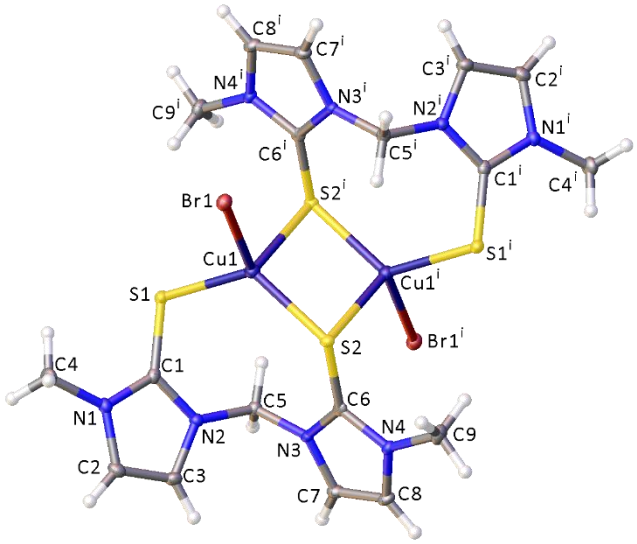


Figure 6 – Molecular structure of $[CuBr\{\kappa^2\text{-}SS,\mu\text{-}S\text{-}\mathbf{SS^{Me}}\}]_2$ (**2**) with atomic labelling scheme depicted. Ellipsoids shown at 50% probability level (^{i} = 1-*x*, -*y*, 1-*z*).

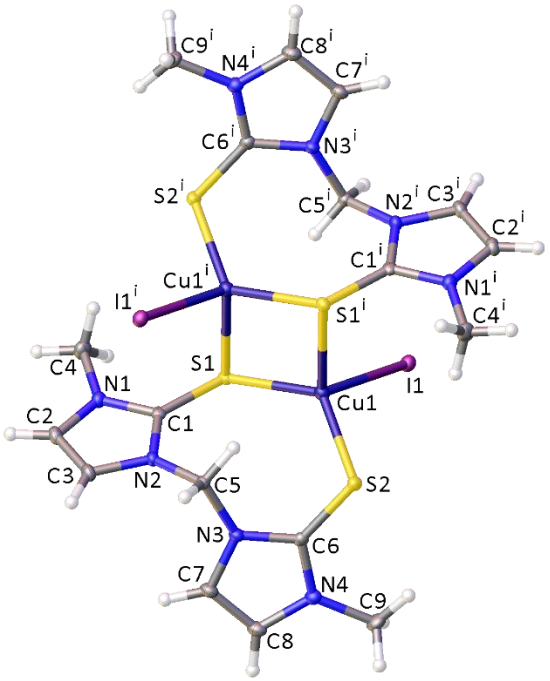


Figure 7 – Molecular structure of [CuI{κ²-*SS*,μ-*S*-**SS^{Me}**}]$_2$ (**3**) with atomic labelling scheme depicted. Ellipsoids shown at 50% probability level (^{i} = 1-*x*, -*y*, 1-*z*).

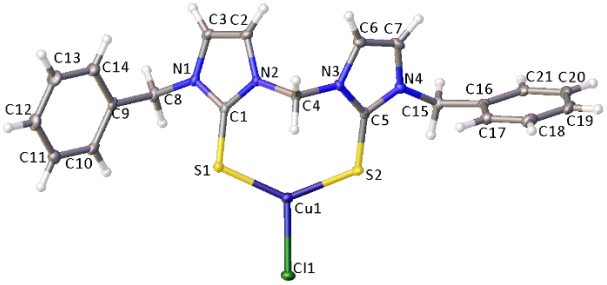


Figure 8 – Molecular structure of [CuCl{κ²-*SS*-**SS^{Bn}**}] (**4**) with atomic labelling scheme depicted. Ellipsoids shown at 50% probability level.

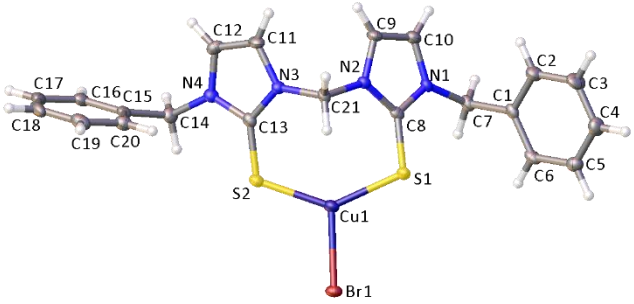


Figure 9 – Molecular structure of [CuBr{κ²-*SS*-**SS^{Bn}**}] (**5**) with atomic labelling scheme depicted. Ellipsoids shown at 50% probability level.

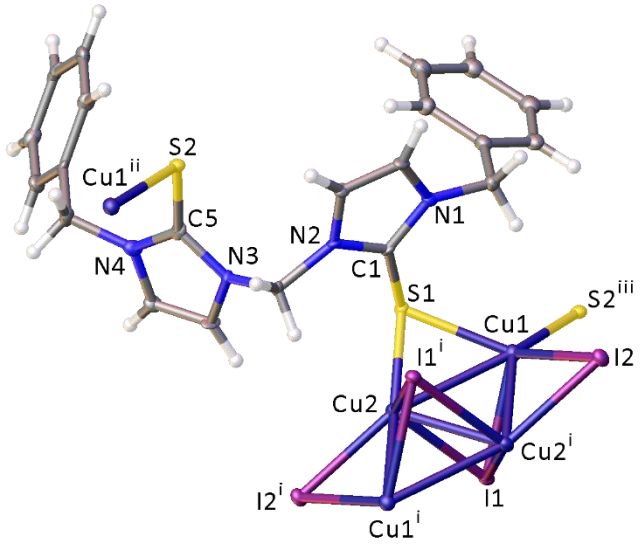


Figure 10 – Structure obtained for complex [CuI{μ-S,κ¹-*S*-**SS^{Bn}**}]$_n$ (**6**). The sulfur atom labelled S1 bridges the Cu1 and Cu2 centres while S2 is bound only to Cu1. An extended network is formed where the **SS^{Bn}** ligand bridges the Cu_4I_4 clusters. Ellipsoids shown at 50% probability level (i = 1-x, 1-y, -z ii = -1+x, +y, +z, iii = 1+x, +y, +z). Selected distances (Å): Cu1–Cu2 2.8162(11), Cu1–Cu2i 2.7504(11), Cu2–Cu1i 2.7505(11), Cu2–Cu2i 2.5897(17), Cu1–I1 2.6678(9), Cu1–I2 2.6736(9), Cu2–I1 2.7931(10), Cu2–I1i 2.8127(9), Cu2–I2i 2.5934(9), Cu2i–I1 2.8127(9), Cu2i–I2 2.5934(9), Cu1–S1 2.4136(18), Cu1–S2iii 2.3393(17), Cu2–S1 2.3278(17), S1–C1 1.721(6), S2–C5 1.699(7).

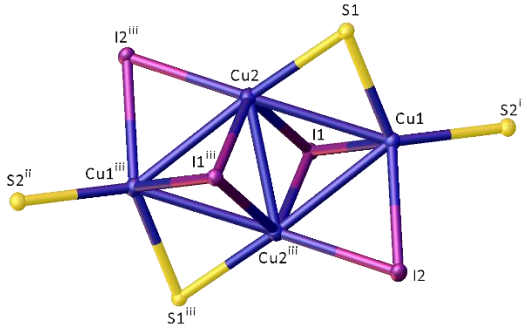


Figure 11 – Core structure obtained for complex **6.** A [Cu_4I_4] cluster coordinated to four **SS^{Bn}** ligands in **6**. Ellipsoids shown at 50% probability level (^{i} = 1+*x*, +*y*, +*z*, ^{ii} = -*x*, 1-*y*, -*z*, ^{iii} = 1-*x*, 1-*y*, -*z*).

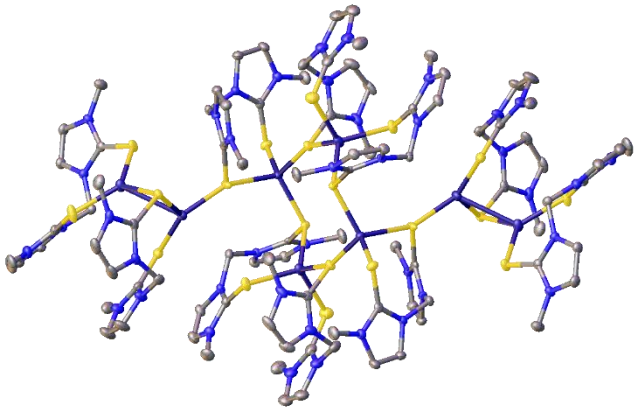


Figure 12 – Crystal structure of **7** obtained from the reaction of $Cu[BF_4]_2.3H_2O$ with **SS^{Me}**. The hydrogen atoms, BF_4 counterions and methanol solvent have been omitted for clarity. Ellipsoids depicted at the 50% probability level.

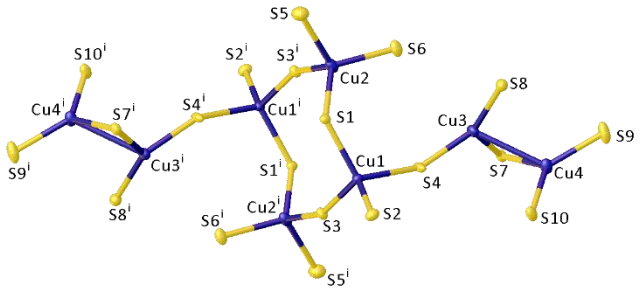


Figure 13 – Core structure indicating the connectivity between the copper and sulfur donors in complex **7**. Ellipsoids shown at 50% probability level (^{i} = 2-*x*, 1-*y*, 1-*z*).

The three copper–halide complexes containing the $\mathbf{SS^{Me}}$ ligand (**1**, **2** and **3**) adopt dinuclear structures containing two copper centres and two ligands. One of the sulfur donor atoms on each ligand bridges the copper centres. The ligand therefore adopts a κ^2-*SS*,μ-*S*-$\mathbf{SS^{Me}}$ coordination mode. As indicated above, this is in contrast to the solution state structure characterisation of these complexes which suggests a symmetrical environment for the $\mathbf{SS^{Me}}$ ligand. It is therefore likely that a mononuclear species exists in solution as indicated in Figure 14. The solid state structures also show short CH–Cu distances (as described below) which do not appear to be present in solution based on the NMR spectroscopic evidence.

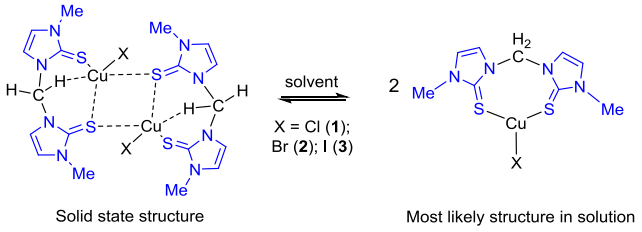


Figure 14 – The difference in the structure in the solid state compared to the one suggested in solution by NMR spectroscopy.

The copper centres in **1**, **2** and **3** adopt similar dinuclear motifs in which the metal centres possess highly distorted tetrahedral geometries with angles ranging between 88.82(4)° – 130.74(4)° for **1**, 103.064(19)° – 125.42(2)° for **2** and 102.145(15)° – 126.707(17)° for **3**. In the case of the bromide and iodide complexes, the widest angle results from the bidentate coordination (S1–Cu–S2) of the $\mathbf{SS^{Me}}$ ligand to copper centre indicating a wide bite angle for this ligand. Within the four membered CuSCuS ring, the copper–copper distances are 3.416(1) Å (**1**), 2.9705(6) Å (**2**) and 3.0131(4) Å (**3**) [*c.f.* Σ_r(CuCu) = 2.64 Å].[14] This distance is well above the range to be considered as metallophillic interactions or d^{10}–d^{10} metal bonding. The short Cu•••Cu distances seem to originate from bridging thione groups rather than any attractive interactions.[15] The Cu–Cu distance is shorter within the bromide structure where the four membered Cu-S-Cu-S ring exhibits a parallelogram motif [103.064(19)° and 76.938(19)°]. The corresponding angles for the iodide complex are 102.145(15)° and 77.855(15)° resulting in a slightly longer Cu–Cu distance as expected from the larger steric demand of this halide. In contrast, the angles found in the chloride example are 88.82(4)° and 91.17(4)° much closer to a rectangular motif resulting in a significantly larger Cu–Cu distance. The dimeric structure adopts a 'zig-zag' type motif where the two $\mathbf{SS^{Me}}$ ligands are located above and below the plane formed by the "CuSCuS" ring (*i.e.* at opposite sides of the parallelogram motif). As indicated above, the three structures show that one of the hydrogen atoms of the methylene units between the thione rings of the $\mathbf{SS^{Me}}$ ligand points towards the copper centre. The Cu---H distances, 2.479 Å for **1**, 2.740 Å for **2** and 2.664 Å for **3,** are too large to indicate any significant interaction as the sum of the covalent radii of copper (1.32) and hydrogen (0.31) is 1.63 Å.[14] The Cu–S distances for the thione unit featuring the terminal non-bridging coordination modes were similar in the bromide and iodide complexes, *cf.* 2.3024(6) Å for **2** and 2.3069(5) Å for **3** [*cf.* Σ_r(CuS) = 2.37 Å].[14] These are similar to distances for the Cu–S terminal thione bonds in the related complex reported by Brumaghim[3p] which lie in the range of 2.2710(16) Å and 2.3067(15) Å. There is a significant difference for the chloride complex **1** where the Cu–S distance is 2.3541(12) Å. The corresponding Cu–S distances involving the bridging mode for all three complexes ranged from 2.3221(6) Å to 2.4602(5) Å. While the Cu–S distances were significantly shorter for the terminal thione than the bridging ones within complexes **2** and **3**, the same is not true for the Cu–S distances in **1** which are 2.4347(13), 2.3462(12) and 2.3541(12) Å. The related copper complex containing the mixed NHC-thione ligand, $\mathbf{CS^{Me}}$, forms a similar dinuclear structure which involves similar four-membered Cu-S-Cu-S rings within a parallelogram motif.[8a] Similar sulfur bridged structures to those observed for **1**, **2** and **3** have also previously been reported by Raper and Lobana in compounds such as [Cu(μ-*S*-$\mathbf{mt^{Me}}$)$_2$(SCN)]$_2$ and [CuX(μ-*S*-$\mathbf{mt^{Me}}$)$_2$(η^1-*S*-$\mathbf{mt^{Me}}$)]$_2$ (where $\mathbf{mt^{Me}}$ = 1-methyl-imidazole-2-thione).[1b,16] Furthermore, in the complex reported by Brumaghim which contains both $\mathbf{mt^{Me}}$ and $\mathbf{SS^{Me}}$ ligands, the bidentate ligand coordinates via a κ^2-*SS* mode while the $\mathbf{mt^{Me}}$ ligands bridge the copper centres.[3p]

Crystal structures were obtained for the correspopnding $\mathbf{SS^{Bn}}$ complexes, **4**, **5** and **6** from acetonitrile solutions. The structures of **4** and **5** revealed mononuclear structures (Figures 8 and 9). This, of course, is in contrast to the three other $\mathbf{SS^{Me}}$ complexes. Interestingly, the corresponding [CuX($\mathbf{CS^{Bn}}$)]$_2$ compounds form dinuclear structures and it appears that the additional sulfur atom within the new complex changes the morphology. Complex **6**, the iodide complex bearing the $\mathbf{SS^{Bn}}$ ligand, gave a different structural motif (Figures 10 and 11). The solid state structures of **4** and **5** reveal a bidentate coordination mode, κ^2-*SS*, of the $\mathbf{SS^{Bn}}$ ligand to the copper metal centres forming eight-membered chelating rings. These isostructural complexes adopt trigonal geometries with angles ranging between 110.66(2)° – 134.28(2)° for **4** and 110.96(3)° – 136.25(3)° for **5**. The sum of the angles around the copper centres equate to 359.95° and 359.96, respectively, indicating that the coordination about the copper centres is essentially planar. The largest angles about the metal centre are found to be the S–Cu–S angles involving the bite angle of the ligand which in these cases are 134.28(2)º and 136.25(3)º, respectively. These angles are significantly larger than those found in the corresponding complexes containing the $\mathbf{SS^{Me}}$ ligand. The larger bite angle presumably precludes the dimer formation which is observed with the former complexes. As a consequence, the binding of the ligand to the copper centre appears to be stronger than found in complexes **1**, **2** and **3**; the copper–sulfur distances are 2.2032(5) Å and 2.2178(5) Å for **4** and 2.2071(2) Å and 2.2129(3) Å for **5**. The positioning of the methylene group is of interest. As with complexes **1**, **2** and **3**, the methylene groups in **4** and **5** appear to point towards the CuX unit. The eight-membered ring adopts a conformation where the five atoms, C=S–Cu–S=C lie on a plane. The N–C–N atoms are positioned above this plane where the CH_2 unit is closer to the copper centre.

The structure obtained for complex **6** was different from the two morphologies described above. In this case, the $\mathbf{SS^{Bn}}$ ligand coordinates via a κ^1-*S* coordination mode for one of the sulfur donors and a μ^2- bridging mode to two copper centres for the other sulfur donor. The copper and iodine centres form Cu_4I_4 cluster motifs[17] which are linked together by the $\mathbf{SS^{Bn}}$ ligands.

In the structure, for each $\mathbf{SS^{Bn}}$ ligand there is one copper and one iodide and the stoichiometry of the overall structure is $[CuI(\mathbf{SS^{Bn}})]_n$. Here, the copper–sulfur distances are 2.3393(17) Å for the bond involving the κ^1-*S* coordination mode to one copper centre and 2.4136(18) Å and 2.3278(17) Å for the μ^2-bridging mode to two copper centres.

Finally, the structure obtained from the reaction of the copper(II) salt, $Cu[BF_4]_2.3H_2O$ with $\mathbf{SS^{Me}}$ showed that a reduction in the oxidation state of the metal centre had occured. The mechanism by which this reduction occurs is currently unknown. The structure exhibits a complicated arrangement of the copper and ligands. It shows four copper centres bridged by four sulfur donors from the ligands to form an eight membered ring structure. Two further copper centres are additionally tethered on either side of the central ring motif via bridging of the thione donors in the $\mathbf{SS^{Me}}$ ligands. In total there are eight copper centres and ten $\mathbf{SS^{Me}}$ ligands within the structure. The S–Cu–S angles across the structure range from 97.49(3)° to 131.34(3)°. The Cu–S distances range from 2.2135(9) Å to 2.4172(8) Å.

Table 2 – A comparison of selected distances (Å) and angles (°) for the $\mathbf{SS^{Me}}$ complexes, **1**, **2** and **3**.

	1	**2**	**3**
Cu-S bonds CuSCuS unit	2.4347(13) / 2.3462(12)	2.4502(6) / 2.3221(6)	2.4602(5) / 2.3325(5)
Cu–S non-bridging thione	2.3541(12)	2.3024(6)	2.3069(5)
Cu-Cu	3.416(1)	2.9705(6)	3.0131(4)
Cu-X	X = Cl; 2.2863(12)	X = Br; 2.4810(4)	X = I; 2.6471(2)
C(1)-S / C(5)-S(6)	1.711(4) / 1.700(4)	1.714(2) / 1.707(2)	1.7121(17) / 1.7057(18)
Cu-H involving methylene unit	2.489	2.740	2.664
internal S-Cu-S within CuSCuS unit	88.82(4)	103.064(19)	102.145(15)
Cu-S-Cu	91.17(4)	76.938(19)	77.855(15)
S-Cu-S within $\mathbf{SS^{Me}}$ ligand	111.59(4)	125.42(2)	126.707(17)
S-Cu-S between two $\mathbf{SS^{Me}}$ ligands	99.56(4)	107.05(2)	108.559(17)
X-Cu-S angles CuSCuS unit	130.74(4) / 112.74(5)	104.182(17) / 107.701(18)	103.899(13) / 105.234(12)
X-Cu-S angle terminal thione	111.07(5)	107.525(19)	108.434(13)
Cu-S-C angles CuSCuS unit	109.24(15) / 118.57(15)	96.83(7) / 120.15(8)	96.19(6) / 119.09(6)
Cu-S-C terminal thione	113.61(15)	104.10(8)	103.80(6)
N-C-N (methylene unit)	111.8(3)	111.65(17)	111.43(14)

Table 3 – A comparison of selected distances (Å) and angles (°) for the $\mathbf{SS^{Bn}}$ complexes, **4** and **5**.

	4	**5**
Cu-S	2.2032(5) / 2.2178(5)	2.2071(9) / 2.2129(5)
Cu-X	X = Cl, 2.2430(5)	X = Br, 2.3731(5)
C-S	1.7035(18) / 1.7012(18)	1.701(3) / 1.705(3)
Cu-H involving methylene unit	2.617	2.595
S-Cu-S	134.28(2)	136.25(3)
X-Cu-S	115.01(2) / 110.66(2)	112.76(3) / 110.96(3)
Cu-S-C	108.31(6) / 115.69(6)	108.45(11) / 114.70(11)
N-C-N (methylene unit)	111.40(14)	111.6(2)

3. Conclusions

In summary, a novel ditopic bis-thione ligand, H_2C(1-benzyl-imidazole-2-thione)$_2$ ($\mathbf{SS^{Bn}}$) was synthesized and fully characterised. The first studies into its coordination chemistry has been carried out on a series of copper–halide complexes. The first copper-halide complexes of the previously studied ligand, H_2C(1-methyl-imidazole-2-thione)$_2$, $\mathbf{SS^{Me}}$ have also been prepared. In addition to the direct synthesis of these complexes, *via* the addition of the corresponding ligand to the copper(I) halides, the complexes $[CuBr(\mathbf{SS^{Me}})]_2$, $[CuI(\mathbf{SS^{Me}})]_2$, $[CuBr(\mathbf{SS^{Bn}})]$ and $[CuI(\mathbf{SS^{Bn}})]_n$ were synthesised via an interesting sulfur atom insertion methodology from the corresponding copper complexes containing the mixed ditopic NHC/thione ligands, $\mathbf{CS^R}$. Single crystals were obtained from all complexes and were characterised by X-ray crystallography. Interestingly, the structures revealed different coordination modes for the $\mathbf{SS^{Me}}$ and $\mathbf{SS^{Bn}}$ ligands. All three copper(I) halide complexes (chloride, bromide and iodide) containing the former ligand exhibited a dinuclear structure bridged by one of the sulfur donors of the $\mathbf{SS^{Me}}$ ligand. This is a new bridging coordination mode to that previously observed for this ligand. Two of the three copper(I) halides gave straightforward mononuclear complexes featuring a κ^2-*SS* coordination mode in the corresponding chloride and bromide complexes containing $\mathbf{SS^{Bn}}$. A different coordination mode was observed for $[CuI(\mathbf{SS^{Bn}})]_n$ where the two sulfur donors where connected to different copper centres, one sulfur donor coordinated with a κ^1-S mode while the other sulfur donor bridged two copper centres. The ligand within the structure was bridged by a Cu_4I_4 cluster. Thus, we have expanded the range of coordination modes of the $\mathbf{SS^R}$ ligands. It is apparent that there is great flexibility in the strength of binding and the degree of coordination modes possible in the coordination of these $\mathbf{SS^{Me}}$ and $\mathbf{SS^{Bn}}$ ligands.

4. Experimental Section

4.1 General Remarks: The synthetic steps to prepare the ligand, $\mathbf{SS^{Bn}}$ and the direct route to prepare the complexes were carried out under aerobic conditions. The synthesis involving the insertion of sulfur into the copper mixed NHC/thione complexes required the reactions to be carried out under a nitrogen atmosphere using standard Schlenk techniques since the precursors are air sensitive. All chemicals and solvents were used as received. For those solvents required for the copper mixed NHC/thione reactions, anhydrous solvents were used. These were kept in Young's flasks under N_2 over molecular sieves (4 Å). The ligand, $\mathbf{SS^{Me}}$ and the complexes $[CuX(\mathbf{CS^R})]_2$ (where X = Br, I; R = Me, Bn) were prepared according to the procedures outlined in reference 8a. ^{1}H NMR spectra were recorded at room temperature on a JEOL Lambda 300 spectrometer operating at 300 MHz, a JEOL ECP 400 spectrometer

operating at 400 MHz or a Bruker Avance III 400 MHz NMR spectrometer. $^{13}C\{^1H\}$ NMR spectra were recorded at room temperature on a JEOL ECP 400 spectrometer or a Bruker Avance III 400 MHz NMR spectrometer. Electrospray Mass Spectra (ESI^+) were recorded on a Bruker Daltonics Apex 4e 7.0T FT-MS mass spectrometer. Infrared spectra were recorded in the region 4000-650 cm^{-1} on a Perkin-Elmer Spectrum 100 FT-IR spectrometer (solid state, powder film). Elemental analyses were performed by the microanalytical laboratory, School of Chemistry, University of Bristol.

4.2 Bis(1-benzyl-imidazole-2-thione)methane, SS^{Bn}

A round bottomed flask equipped with a stirring bar was charged with *N,N'*-methylenebis(3-methyl)imidazolium diiodide[9] (4.00 g; 6.85 mmol) and methanol (35 mL) to give a clear solution. Sulfur (0.449 g, 13.7.0 mmol, 2.0 equiv.) and potassium carbonate (0.959 g, 6.85 mmol, 1.0 equiv.) were added under stirring to the solution to give a suspension. The mixture was heated to reflux for 24 h. It was allowed to cool to room temperature and all volatiles removed. The residue was extracted with chloroform (100 mL), filtered and the filtrate evaporated to dryness. The residue was redissolved in a minimum of dichloromethane. Addition of methanol precipitated the product as a white solid (2.51 g, 6.39 mmol, 93%). ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 5.22 (s, 4H, CH_2Ph), 6.41 (s, 2H, NCH_2N), 6.51 (d, $^3J_{HH}$ = 2.5 Hz, 2H, C*H*=CH), 7.35 (m, 10H, *o*/*m*/*p*-C_6H_5), 7.64 (d, $^3J_{HH}$ = 2.5 Hz, 2H, CH=C*H*). $^{13}C\{^1H\}$-NMR (75 MHz, $CDCl_3$): δ = 51.4 (*C*H_2Ph), 56.2 (N*C*H_2N), 116.5 (*C*H=CH), 119.0 (CH=*C*H), 128.4 (*o*/*p*-C_6H_5), 129.1 (*m*-C_6H_5), 135.2 (*i*-C_6H_5), 164.0 (C=S). IR (cm^{-1}): 3135.6, 3089.5, 2942.0, 1567.4, 1445.3, 1412.3, 1374.5, 1302.8, 1187.4, 1078.1, 909.8, 742.9, 692.6. MS (ESI^+), m/z 415.1 [(**SS^{Bn}**) + Na]$^+$, 391.16 [(**SS^{Bn}**) – H]$^+$. Elemental Analysis: Calc. for $C_{21}H_{20}N_4S_2$: C: 64.26; H: 5.14; N:14.27; Found: C: 64.39; H: 5.29; N 14.13.

[CuCl(SS^{Me})]$_2$ (1)

CuCl (50 mg, 0.50 mmol) was dissolved in acetonitrile (80 mL). A solution of **SS^{Me}** (120 mg, 0.50 mmol) in acetonitrile (30 mL) was added in one portion. The solutions were mixed and stirred overnight, resulting in an off-white precipitate. The solid was isolated by filtration and rinsed with acetonitrile. The resulting solid was dried to give **1** as an off-white solid. Yield = 76 mg (0.11 mmol, 45 %). ^{1}H NMR (*d*$_6$-DMSO, 400 MHz) δ 3.41 (6 H, s, NCH_3), 6.49 (2 H, s, NCH_2), 7.32 (2 H, d, $^3J_{HH}$ = 2.5 Hz, NC*H*CHN), 7.57 (2 H, d, $^3J_{HH}$ = 2.5 Hz, NCHC*H*N). $^{13}C\{^1H\}$ NMR (*d*$_6$-DMSO, 100 MHz) δ 35.5 (NCH_3), 56.5 (NCH_2), 118.8 (NC*H*CHN), 121.0 (NCHC*H*N), 158.2 (CS). MS (ESI^+), m/z 643 [Cu_2Cl(**SS^{Me}**)$_2$]$^+$, 543 [Cu(**SS^{Me}**)$_2$]$^+$, 303 [Cu(**SS^{Me}**)]$^+$. IR: 3154, 3122, 3089, 2968, 2929, 1692, 1607, 1574. Anal. Found: C, 31.84; H, 3.52; N, 15.72. Calcd for $C_9H_{12}ClCuN_4S_2$: C, 31.73; H, 3.55; N, 16.10.

[CuBr(SS^{Me})]$_2$ (2)

Direct route CuBr (72 mg, 0.50 mmol) was dissolved in acetonitrile (30 mL). A solution of **SS^{Me}** (120 mg, 0.50 mmol) in acetonitrile (30 mL) was added in one portion. The solutions were mixed and stirred overnight, resulting in an off-white precipitate. The solid was isolated by filtration and rinsed with acetonitrile. The resulting solid was dried to give **2** as an off-white solid. Yield = 137 mg (0.178 mmol, 71 %). **Sulfur insertion route** [CuBr(**CS^{Me}**)]$_2$ (70.4 mg, 0.10 mmol) was partially dissolved in acetonitrile (20 mL) in a Schlenk flask. To this was added an excess of sulfur (64 mg, 2.00 mmol per sulfur). The mixture was stirred at 50 °C for 3 h after which time the mixture was diluted with 10 mL of acetonitrile and filtered. The volume of the filtrate was reduced to 2 mL and diethyl ether was added to precipitate an off-white solid. The solid was isolated by filtration, washed with a portion of diethyl ether and dried under reduced pressure. Yield = 42 mg (0.055 mmol, 55 %). ^{1}H NMR (*d*$_3$-MeCN, 300 MHz) δ 3.54 (6 H, s, NCH_3), 6.43 (2 H, s, NCH_2), 6.95 (2 H, d, $^3J_{HH}$ = 2.5 Hz, NC*H*CHN), 7.27 (2 H, d, $^3J_{HH}$ = 2.5 Hz, NCHC*H*N); (*d*$_6$-DMSO, 400 MHz) δ 3.48 (6 H, s, NCH_3), 6.56 (2 H, s, NCH_2), 7.36 (2 H, d, $^3J_{HH}$ = 2.5 Hz, NC*H*CHN), 7.60 (2 H, d, $^3J_{HH}$ = 2.5 Hz, NCHC*H*N). $^{13}C\{^1H\}$ NMR (*d*$_6$-DMSO, 100 MHz) δ 35.6 (NCH_3), 56.2 (NCH_2), 119.0 (NC*H*CHN), 121.2 (NCHC*H*N), 157.7 (CS). MS (ESI^+), m/z 831 [Cu_3Br_2(**SS^{Me}**)$_2$]$^+$, 687 [Cu_2Br(**SS^{Me}**)$_2$]$^+$), 543 [Cu(**SS^{Me}**)$_2$]$^+$, 303 [Cu(**SS^{Me}**)]$^+$. IR: 3157, 3130, 3110, 3095, 2982, 1709, 1655, 1603, 1576. Anal. Found: C, 28.29; H, 3.52; N, 14.51. Calcd for $C_9H_{12}ClCuN_4S_2$: C, 28.16; H, 3.15; N, 14.60.

[CuI(SS^{Me})]$_2$ (3)

Direct route CuI (95 mg, 0.50 mmol) was dissolved in acetonitrile (25 mL). A solution of **SS^{Me}** (120 mg, 0.50 mmol) in acetonitrile (30 mL) was added in one portion. The solutions were mixed and stirred overnight, resulting in an off-white precipitate. The solid was isolated by filtration and rinsed with acetonitrile. The resulting solid was dried to give **3** as an off-white solid. Yield = 203 mg (0.236 mmol, 94 %). **Sulfur insertion route** [CuI(**CS^{Me}**)]$_2$ (79.6 mg, 0.10 mmol) was partially dissolved in acetonitrile (20 mL) in a Schlenk flask. To this was added an excess of sulfur (32 mg, 1.00 mmol per sulfur). The mixture was stirred at 70 °C for 3 h after which time the mixture was diluted with 10 mL of acetonitrile and filtered. The volume of the filtrate was reduced to 2 mL and diethyl ether was added to precipitate an off-white solid. The solid was isolated by filtration, washed with a portion of diethyl ether and dried under reduced pressure. Yield = 38 mg (0.044 mmol, 44 %). ^{1}H NMR (*d*$_6$-DMSO, 400 MHz) δ 3.58 (6 H, s, NCH_3), 6.72 (2 H, s, NCH_2), 7.44 (2 H, d, $^3J_{HH}$ = 2.5 Hz, NC*H*CHN), 7.65 (2 H, d, $^3J_{HH}$ = 2.5 Hz, NCHC*H*N). $^{13}C\{^1H\}$ NMR (*d*$_6$-DMSO, 100 MHz) δ 36.2 (NCH_3), 56.6 (NCH_2), 119.7 (NC*H*CHN), 121.9 (NCHC*H*N), 155.6 (CS). MS (ESI^+), m/z 925 [Cu_3I_2(**SS^{Me}**)$_2$]$^+$, 735 [Cu_2I(**SS^{Me}**)$_2$]$^+$, 543 [Cu(**SS^{Me}**)$_2$]$^+$, 303 [Cu(**SS^{Me}**)]$^+$. IR: 3159, 3115, 3099, 2972, 2938, 1680, 1656, 1631, 1572. Anal. Found: C, 25.28; H, 2.80; N, 12.56. Calcd for $C_9H_{12}ICuN_4S_2$: C, 25.09; H, 2.81; N, 13.01.

[CuCl(SS^{Bn})] (4)

A round-bottomed flask equipped with a stirring bar was charged with the ligand, **SS^{Bn}** (0.1503 g; 0.38 mmol) and acetonitrile (10 mL) to give a white milky suspension. Anhydrous CuCl (0.0378 g, 0.38 mmol) was added in one portion under vigourous stirring to give a pale green mixture which became briefly transparent after a few minutes. The mixture was stirred overnight to give a white precipitate; it was sonicated for a few seconds and further stirred for 30 min. Diethyl ether (10 mL) was added and stirring was continued for 5 min to give the product as a white powder which was filtered, washed with diethyl ether (5 mL) and dried in air. Yield = 0.1394 g, 0.284 mmol, 75%). ^{1}H-NMR (300 MHz, *d*$_6$-DMSO): δ = 5.16 (s, 4H, PhCH_2), 6.46 (s, 2H, NCH_2N), 7.29 (s, 10H, 2 x *o*/*m*/*p*-C_6H_5), 7.40 (s, 2H, CH=C*H*), 7.57 (overlapping signals, 2H, C*H*=C*H*). $^{13}C\{^1H\}$ NMR (*d*$_6$-DMSO, 100 MHz) δ = 50.4 (*C*H_2Ph), 56.4 (N*C*H_2N), 119.0 (*C*HCH), 119.6 (CH*C*H), 127.8 (overlapping, *m*/*p*-C_6H_5), 128.5 (*o*-C_6H_5), 135.6 (*i*-C_6H_5), 158.2 (C=S). MS (ESI^+), m/z 847 [Cu(**SS^{Bn}**)$_2$]$^+$, 455 [Cu(**SS^{Bn}**)]$^+$. IR (cm^{-1}): 3390.3, 3093.4, 1672.7, 1570.9, 1496.2, 1451.8, 1408.5, 1354.5, 1230.6, 1190.5, 1166.0, 1079.6, 1028.5, 847.1, 693.6. Elemental analysis: Calc. for $C_{21}H_{20}ClCuN_4S_2$: C: 51.31; H: 4.10; N: 11.40. Found: C: 51.16; H: 4.03; N: 11.44.

[CuBr(SS^{Bn})] (5)

Direct route A round-bottomed flask equipped with a stirring bar was charged with the ligand, **SS^{Bn}** (0.1503 g; 0.383 mmol) and acetonitrile (10 mL) to give a white milky suspension. Anhydrous CuBr (0.0555 g, 0.38 mmol) was added in one portion under vigourous stirring to give a white suspension which became briefly transparent after a few minutes. The mixture was stirred overnight to give an off-white precipitate; it was sonicated for a few seconds and further stirred for 30 min. Diethyl ether (10 mL) was added and stirring was continued for 5 min to give the product as a white powder which was filtered, washed with diethyl ether (5 mL) and dried in air (0.1802 g, 0.334 mmol, 88%). **Sulfur insertion route** [CuBr(**CS^{Bn}**)]$_2$ (103

mg, 0.102 mmol) was partially dissolved in acetonitrile (20 mL) in a Schlenk flask. To this was added an excess of sulfur (66 mg, 2 mmol per sulfur). The mixture was stirred at 70 °C for 5 h after which time the mixture was diluted with 10 mL of acetonitrile and filtered. The residue was extracted with acetonitrile (2 × 10 mL). The solvent of the combined organic phases was removed by oil pump vacuum and the off-white solid dried under reduced pressure. Yield = 72.6 mg (0.135 mmol, 66 %). ^{1}H-NMR (300 MHz, d_6-DMSO): δ = 5.22 (s, 4H, PhCH_2), 6.66 (s, 2H, NCH_2N), 7.32 (s, 10H, 2 x C$_6H_5$), 7.50 (overlapping signal, 2H, CH=CH), 7.70 (overlapping signal, 2H, CH=CH). ^{13}C{^{1}H} NMR (d_6-DMSO, 100 MHz) δ 50.3 (*C*H$_2$Ph), 56.2 (N*C*H$_2$N), 118.9 (*C*HCH), 119.2 (CH*C*H), 127.9 (overlapping, *m*/*p*-*C*$_6$H$_5$), 128.6 (*o*-*C*$_6$H$_5$), 135.9 (*i*-*C*$_6$H$_5$), 159.4 (C=S). IR (cm^{-1}): 3390.3, 3092.1, 1569.7, 1495.9, 1451.8, 1408.1, 1231.2, 1190.4, 959.6, 704.5, 671.6. MS (ESI$^+$), m/z 991 [Cu$_2$(**SS^{Bn}**)$_2$Br]$^+$, 847 [Cu(**SS^{Bn}**)$_2$]$^+$, 455. [Cu(**SS^{Bn}**)]$^+$. Elemental analysis: Calc. for C$_{21}$H$_{20}$BrCuN$_4$S$_2$: C: 47.06; H: 3.76; N: 10.45. Found: C: 46.96; H: 3.81; N: 10.40.

[CuI(SS^{Bn})] (6)

Direct route A round-bottomed flask equipped with a stirring bar was charged with the ligand, **SS^{Bn}** (0.1504 g; 0.383 mmol) and acetonitrile (10 mL) to give a white milky suspension. Anyhydrous CuI (0.073 g, 0.383 mmol) was added in one portion under vigourous stirring to give a pale green mixture which became transparent after a few minutes. The mixture was stirred overnight to give a white precipitate; it was sonicated for a few seconds and further stirred for 30 min. Diethyl ether (10 mL) was added and stirring was continued for 5 min to give the product as an off-white powder which was filtered, washed with diethyl ether (5 mL) and dried in air (0.1440 g, 0.247 mmol, 64%). **Sulfur insertion route** [CuI(**CS^{Bn}**)]$_2$ (110.0 mg, 0.10 mmol) was partially in acetonitrile (20 mL) in a Schlenk flask. To this was added an excess of sulfur (64 mg, 2.00 mmol per sulfur). The mixture was stirred at 70 °C for 3 h which time the mixture was diluted with 10 mL of acetonitrile and filtered. The volume of the filtrate was reduced to 2 mL and diethyl ether was added to precipitate and off-white solid. The solid was isolated by filtration, washed with a portion of diethyl ether and dried under reduced pressure. Yield = 66 mg (0.11 mmol, 57%). ^{1}H-NMR (300 MHz, d_6-DMSO): δ= 5.22 (s, 4H, PhCH_2), 6.65 (s, 2H, NCH_2N), 7.29 (m, 10H, C$_6H_5$), 7.46 (d, $^{3}J_{HH}$ = 2.5 Hz, 2H, CH=CH), 7.67 (d, $^{3}J_{HH}$ = 2.5 Hz, 2H, CH=CH). ^{13}C{^{1}H} NMR (d_6-DMSO, 100 MHz) δ 50.7 (*C*H$_2$Ph), 55.5 (N*C*H$_2$N), 120.2 (*C*HCH), 120.8 (CH*C*H), 128.5 (*o*-*C*$_6$H$_5$), 128.6 (*p*-*C*$_6$H$_5$), 129.2 (*m*-*C*$_6$H$_5$), 136.0 (*i*-*C*$_6$H$_5$), 157.5 (C=S). IR: 3390.6, 3092.8, 1568.0, 1495.3, 1408.0, 1231.7, 1077.5, 1028.1, 956.4, 705.0 cm^{-1}. MS (ESI$^+$), m/z 1039 [Cu$_2$I(**SS^{Bn}**)$_2$]$^+$, 847 [Cu(**SS^{Bn}**)$_2$]$^+$, 455 [Cu(**SS^{Bn}**)]$^+$. Elemental analysis: Calc. for C$_{21}$H$_{20}$CuI$_2$N$_4$S$_2$: C: 32.61; H: 2.61; N: 7.24. Found: C: 32.66 ; H: 2.63; N: 7.22.

General procedure for the conversion of [CuX(CS^{R})] into [Cu(SS^{R})X] in d$_6$-DMSO

An nmr tube was charged with the copper complex [CuX(**CS^{R}**)]$_2$ and elemental sulfur. The system was placed under vacuum for a few minutes and refilled with a nitrogen atmosphere three times. Degassed dmso-d_6 (0.5 mL) was added to give a yellow suspension. The mixture was immersed in an oil bath at 80 °C and analysed by ^{1}H NMR spectroscopy. The results for each complex are outlined below.

[CuBr(SS^{Me})]$_2$: Using [CuBr(**CS^{Me}**)]$_2$ (10.9 mg, 0.015 mmol) and elemental sulfur (11.4 mg, 0.36 mmol per sulfur). This required 50 min for complete conversion to complex **2**.

[CuI(SS^{Me})]$_2$: Using [CuI(**CS^{Me}**)]$_2$ (10.1 mg, 0.013 mmol) and elemental sulfur (10.6 mg, 0.33 mmol per sulfur). This required 30 min for complete conversion to complex **3**.

[CuBr(SS^{Bn})]: Using [CuBr(**CS^{Bn}**)]$_2$ (5 mg, 0.005 mmol) and elemental sulfur (3.2 mg, 0.1 mmol per sulfur). The reaction was allowed to stir at 80 °C for 2 h after which time complete conversion to complex **5** was confirmed.

[CuI(SS^{Bn})]$_n$: Using [CuI(**CS^{Bn}**)]$_2$ (10.7 mg, 0.019 mmol) and elemental sulfur (13.9 mg, 0.39 mmol per sulfur). This required 30 min for complete conversion to complex **6**.

Crystallography

X-ray diffraction studies were carried out on the complexes **1**, **2**, **3**, **4**, **5**, **6** and **7** at 100(2) K on a Bruker APEX II diffractometer using graphite monochromised Mo-K$_\alpha$ radiation (λ = 0.71073 Å). Data collections were performed using a CCD area detector from a single crystal mounted on a glass fibre. Using Olex2[18], the structures were solved by direct methods in ShelXS-1997[19] and refined by least squares minimisation against F^2 in ShelXL-2015[20]. Crystal structures and refinement data are given in Tables S1 and S2 in the supplementary information. Single crystals of complexes **1** - **6** were obtained by slow diffusion of acetonitrile solutions of the corresponding copper(I) salts into acetonitrile solutions of the **SS^{Me}** or **SS^{Bn}** ligands. Single crystals of complex **7** were obtained by slow diffusion of a methanolic solution of copper(II) tetrafluoroborate hydrate to a dichloromethane solution of **SS^{Me}**. The crystals of **7** contained two molecules of methanol within the structure per complex. A suitable crystal from each sample was selected and placed on the diffractometer. Anisotropic parameters, bond lengths and (torsion) angles for these structures are available from the cif file which can be found in the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. The corresponding CCDC codes for complexes **1** – **7** are 1539313 - 1539319.

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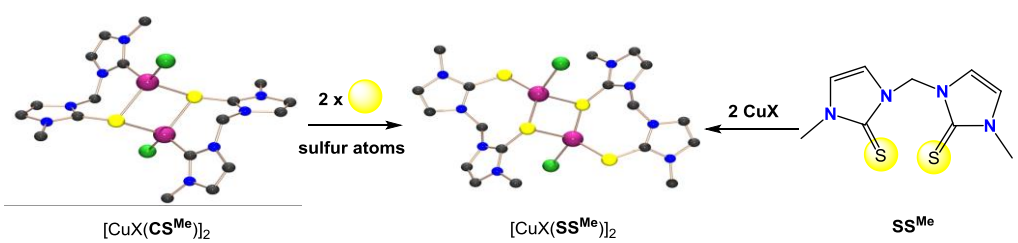
Graphical Abstract

Sulfur atom insertion into a copper-NHC bond vs a direct route



$[CuX(CS^{Me})]_2$ $[CuX(SS^{Me})]_2$ SS^{Me}